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USE OF STATISTICAL TECHNIQUES IN CHEMICAL ANALYSIS AND PROCESS CONTROL

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USE OF STATISTICAL TECHNIQUES IN CHEMICAL ANALYSIS

by

R. Sutarno* and J. L. Dalton**

Abstract

The Division of Nuclear Fuel Cycle of the International Atomic Energy Agency requested the assistance of CANMET in the preparation of a manual on the analytical chemistry of the uranium mining and milling industry. Several reports on various analytical methods have been prepared by the staff of the Chemical Laboratory for this request. This report is intended as a general overview of statistical considerations for the analytical chemistry manual.

Key words: Statistics, quality control, process control.

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UTILISATION DES STATISTIQUES TECHNIQUES DANS L'ANALYSE CHIMIQUE

par

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Résumé

La Division du recyclage des combustibles nucléaires de L'Agence internationale de l'énergie atomique a demandé l'aide de CANMET pour la préparation d'un manuel portant sur la chimie analytique dans les industries d'exploitation et de broyage de l'uranium. Par conséquent, le personnel du Laboratoire de chimie a rédigé plusieurs documents sur les différentes méthodes analytiques. Le présent rapport comprend un exposé général sur les théories statistiques qu'il faudra considérer lors de la rédaction du manuel de chimie analytique.

Mots-clé : Statistique, contrôle de la qualité, régulation du procédé

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1. Introduction

Application of statistics to process industries is commonly associated with "quality control". Quality control is necessary because the product of a process, let it be manufacturing , chemical or measurement is, in general, not consistent with the target value even if all variables have been completely controlled. The fluctuation of these results that can not be attributed to any known cause is usually called "random (statistical) fluctuation". This fluctuation can not be completely eliminated, but at a cost, it can be decreased to an acceptable level. It can occur at various steps of the process. To illustrate this point, let us consider a process for conversion of uranium ore concentrate to UO_2 suitable for fuel fabrication. The objective is to produce UO_2 at a desired concentration (purity); let us say A% UO_2. Ideally the process should produce powder containing exactly A% UO_2 batch after batch, day after day. In practice, however, this ideal condition never happens. The plant produces powder with UO_2 content varying anywhere between A - ϕ% to A + ν% with the average over a long period of time of perhaps A - δ%. Thus in the long run the plant misses its target by δ% and fluctuates from day to day to the extent of $\nu + \phi$%. In statistical terms the value of δ is called the "bias" of the process and the magnitude of $\nu + \phi$ is called the range of the process variation, an expression of precision. The magnitudes of the bias and precision can only be estimated; they are not exact because of the existence of various errors during the measurement (analysis) of the powder. These measurement errors consist of both random and systematic errors. Furthermore, since in general it is not possible to

analyze the whole stock of the powder, it is necessary to obtain a "representative" sample for analysis. Thus additional error due to sampling is introduced at this stage.

The purpose of the application of statistical methodology to this process is to help analyze and hopefully control these errors. This chapter describes briefly what statistical methodology can offer to achieve this objective. The ISO standards handbook[1] is a useful reference for supplementary reading.

2. Frequency distribution

For the application of statistical methods, the process can be represented by the following basic model:

$$x_i = \mu + B + e_i \qquad (1)$$

where:

x_i = process result at any given time.
μ = target value (accepted reference value).
B = bias of the process (systematic error).
e_i = statistical (random) error.

For a given process at steady state, both μ and B are constant. Both e_i and x_i are random variables, assumed to follow a normal frequency distribution with the same variance and means of zero and $(\mu + B)$ respectively. Thus

$$e_i = N\{0,\sigma\}$$

$$x_i = N\{\mu + B,\sigma\}$$

The normality assumption used in most statistical methodology is usually sufficient to represent a wide variety of processes by reason of (a) that according to the "central limit" theory, the distribution of a mean of random variable tends to be more normal

than the distribution of the variable itself and (b) in general one is concerned only with the tail of the distribution, so deviation from normality does not have a serious effect on the inference taken from the process results. In the case where the distribution of the process results clearly deviates from normality, the data often can be transformed to make them closer to a normally distributed variable. For example in the case of the distribution of concentration of respirable dust particles in uranium mines, a logarithmic transformation was found to be suitable.

3. Accuracy

Accuracy of a process is a measure of how close the process can consistently meet the target. In the case of the chemical process the target value is definable by the operator, i.e. the quantity of the product with the predefined characteristics. In the case of a chemical analysis the ultimate target is to determine the "true value". The problem here is that the "true value" is never known although it may conceptually exist. For this reason, the true value is usually replaced by a reference value. Thus practically, the accuracy of the measurement process is defined as the measure of the closeness of the results of the measurement process to a reference value, such as the certified value given for a reference material.

Two components make up the accuracy of a process: precision and trueness.

3.1. Precision

Precision is a measure of the consistency of a process. It is not a measure of how close the process can meet the target value. Unfortunately, the term precision is sometimes erroneously considered as identical with the term "accuracy".

Quantitatively, precision is expressed in term of deviation from the mean. One of the most common measures of precision is the standard deviation.

$$\sigma = [\sum_{1}^{n}(x_i - \bar{x})^2/(n-1)]^{1/2} \qquad (2)$$

$$\bar{x} = \sum_{1}^{n} x_i/n \qquad (3)$$

where:

x_i is an individual result

$\bar{x}$ is the mean of results

n is the number of results

For a normally distributed variable, this precision measure means that there is approximately a 68% chance (two out of three) that in the absence of bias the value of x_i will be within the standard deviation from its true value, i.e.

$$Pr\{\mu - \sigma \leq x_i \leq \mu + \sigma\} = 0.68 \qquad (4)$$

It is important to note that all x_i must be obtained under the same and well defined conditions. Usually there is a qualifying subscript to define a particular σ. For example σ_r signifies repeatability standard deviation, i.e., all x_i's are obtained under repeatability conditions. This quantity is not the same as

σ_R, reproducibility standard deviation, where all x_i's are obtained under reproducibility conditions[2]. In many cases precision is expressed in terms of a confidence interval with higher probability, usually 95% instead of 68%, by introducing a multiplying factor. Thus

$$Pr\{\mu - k\sigma \leq x_i \leq \mu + k\sigma\} = 0.95 \qquad (5)$$

where k is a factor for adjusting the probability level.

As mentioned previously, statistical fluctuation can be reduced, at a cost, to a desired level. For a chemical process this reduction is often done by mixing batches of the product (powder). For a measurement process, this reduction is normally done by performing replications and averaging the results. The following relation is very useful tool:

$$\sigma_m = \sigma/\sqrt{n} \qquad (6)$$

where σ_m is the standard deviation of the mean of n results.
A further benefit of replication is that the distribution of the means is usually closer to "normal" than the distribution of the individual results.

To avoid misunderstanding, a precision expression such as standard deviation should only be used to describe the precision of a variable from a well defined population. For example, a standard deviation of individual analytical results must be computed from equation (2) using individual results as x_i's. The standard deviation of means of two results (paired results) must be computed using the same formula replacing x_i with means of two results. Other conditions such as the origin of the data must

also be defined; thus the standard deviation between-laboratory (σ_R) should not be mixed up with the standard deviation within-laboratory (σ_r) etc.

3.2. Trueness

Trueness of a process is a measure of how close the process can, in the long run, meet its target value. In the measurement process, trueness is defined as "the closeness of agreement between the average value obtained from a large series of observations and an accepted reference value"[2]. Quantitatively, the trueness is usually expressed in terms of "bias", δ.

$$\delta = E\{x_i\} - \mu \qquad (7)$$

where:

$E\{x_i\}$ = expected value of x_i

μ = the reference value

Experimentally, the expected value of x_i is estimated by the long term mean of x_i:

$$E\{x_i\} = \Sigma x_i / n \qquad (8)$$

4. Source of errors

In order to assess the performance of a process, one must perform a measurement of the predefined attribute of the process. It is inevitable that the decision made will be affected by the accuracy of the measurement process. In most cases, the overall measurement process involves a sampling process, preparing the sample into a suitable form/quantity for the measurement procedure, and the measurement procedure itself. Potentially, each of

these processes will introduce error. All of these errors consist of two components: systematic/bias and random/statistical.

4.1. Sampling

A sample is a portion of the material (population) to be taken for the purpose of providing information on the population. The accuracy of the conclusion drawn from a sample depends on the variability of the material. For homogeneous materials, a sample taken from any portion of the population (batch) will represent the population accurately; for heterogeneous materials, careful procedures must be followed in order to take a proper sample with a certain desired accuracy. For some materials, sampling error is an important component of overall measurement error.

Another factor to be considered in sampling is the objective, i.e. what information is required on the population. Does one require only the average characteristic or the variability as well? What type of characteristics are required? Some characteristics have a tendency to have greater variation than others; in many cases particle size of ores has greater variation than composition.

4.2. Sample preparation

In many cases, a sample taken directly from the population is unsuitable for the measurement procedure because of its quantity, size, form etc. In this situation, it is necessary to use a sample preparation procedure and prepare the sample (by grinding, mixing etc.) prior to the measurement procedure. The error intro-

duced at this stage is usually referred to as the preparation error. As in the case of sampling error, the preparation error consists of two components: systematic and random components. The systematic component can be controlled by physical improvement of the equipment while the random component can be controlled by the preparation of multiple samples.

4.3. Measurement error

This is the component of error generated by the measurement itself. In the case of chemical analysis for example, this error may originate from weighing, titration, instrumental error etc. As indicated above, this error consists of both systematic and random components and depends on the nature of the measurement. This error could be smaller (chemical analysis of ores) or greater than the other components (error on the tumbler test of iron ore is comparable in magnitude with that of the sampling error).

4.4. Overall measurement error

The overall measurement error is the total of the error components mentioned above. It is accepted that the variances (σ^2) of the above error components are additive. Thus

$$\sigma_{SDM} = (\sigma_S^2 + \sigma_D^2 + \sigma_M^2)^{1/2} \qquad (9)$$

where:

σ_{SDM} = overall measurement standard deviation

σ_S = sampling standard deviation

σ_D = preparation standard deviation

σ_M = measurement standard deviation

Note: The partition between the sampling and sample preparation error is completely arbitrary. If it is desired they can be combined into one error.

5. Statistical inference

Before one conducts an experiment, one must clearly define the objectives. For example, one may conduct an experiment to see if process B will produce the same results as process A. In order to define this objective, one must first clearly define "what does it mean by the results of two processes being equal"; also what is the degree of difference between the two processes that will matter. In statistical terms, the results of two processes are considered to be the same, if they can be assumed to come from the same frequency distribution. The results of two processes are considered to be different if they can be shown to come from two different distributions. The difference between the parameter under consideration (usually mean or variance) of these two distributions must be greater than a certain value.

Before conducting the experiment, the experimenter must hypothesize the phenomena under consideration, i.e., is process A equal to process B; alternatively process A is not equal to process B. The former hypothesis is usually referred to as the null hypothesis (H_o) and the later as the alternative hypothesis (H_1). The outcome of the experiment will help the experimenter to decide which of these two hypotheses is true. Because of the inevitable statistical error, one will expect that a wrong decision is occasionally made. Although this error can not be eliminated completely, one may be able to control the probability of committing it. There are two types of error in this respect:

Error type I

Error type I is an error committed when the experimenter rejects his null hypothesis, when in reality it is true. The probability of committing this error type, usually designated as α, is called the significance level.

In the above example, error type I is the error that is committed by the experimenter that concludes that the results of processes A and B are different, when in fact the results of these two processes are not different.

Error type II

Error type II is an error committed when the experimenter accepts his null hypothesis, when in reality his hypothesis is false. The probability of committing this error, usually designated as β, depends on the alternative hypothesis, H_1, (the difference of the two distributions that the experimenter considers significant according to his requirements); β can be calculated only if this alternative hypothesis is adequately specified.

In the above example, error type II is the error committed by the experimenter in concluding that the results of processes A and B are equal, when in fact the two processes produce results that differ by an amount greater than that given by the specified alternative hypothesis.

The values of both α (also known as the producer's risk) and β (consumer's risk) are important considerations in the design of an experiment.

Figure 1, which is a histogram for four hypothetical normal distributions, is a graphical representation of the acceptance/-rejection regions and the associated errors. The B and C distributions represent the range of the acceptable parameters for the process under investigation. Ideally, B and C would be one distribution but, in practice, a range of distributions may occur. A and D distributions represent the alternate distributions. The target value for the process is in the range $a_2 \leq x \leq a_1$, the experimental acceptance region is in the region $L_L \leq x_i \leq U_L$ and the rejection regions are $x_i < L_L$ and $x_i > U_L$. Decision errors are often committed when x_i fall around the L_L and U_L boundaries. The probability of committing a Type I error is represented by the area of distribution C that is greater than U_L or less than L_L for distribution B. Similarly the probability of committing a Type II error is represented by the area of distribution D that is less than U_L or greater than L_L for distribution A. The length of M_1' increases as the magnitude of error in the decision making process decreases. For a fixed value of M_1' the error can be reduced also by performing more measurements or increasing the size of the sample and thus narrowing the width of these distributions, thus decreasing the overlaps.

6. Control charts

A control chart is a chart, with upper and/or lower control limits, on which values of some statistical measures (such as mean, range etc.) for a series of samples or sub-groups are plotted. The chart frequently shows a central line to assist detec-

tion of a trend of plotted values toward either control limit. A control chart is usually used as a graphical method to see if the process is operating satisfactorily i.e. that the process variation is random in nature and that the process is in state of "statistical control". A control chart is a "life" chart; it should be updated periodically to see if there is a change in the process. The most popular and simplest control charts are Shewhart charts for the mean and range of the process. Both charts are based on the assumption that the variables are normally distributed.

Mean Chart

As its name implies, this chart is use to monitor the mean of the process i.e. if the mean is constant or follows a trend. Figure 2 shows an example of this chart. The vertical axis represents the process variable (results) and the horizontal axis represent time. It has a central line, which is the mean of the process. The chart usually has an upper warning limit (UWL), lower warning limit (LWL), upper control limit (UCL) and lower control limit (LCL). In theory, the operator should define these limits in accordance with his need. Customarily, however, they are defined as follows: UWL and LWL are defined as the limits within which 95% of the process results will fall and UCL and LCL are defined as the limits within which 99% of the process results will fall.

Thus:

Central line: $\bar{\bar{x}}$

UWL	: $\bar{\bar{x}} + 2\sigma$	LWL	: $\bar{\bar{x}} - 2\sigma$
UCL	: $\bar{\bar{x}} + 3\sigma$	LCL	: $\bar{\bar{x}} - 3\sigma$
$\bar{\bar{x}}$	: $\Sigma x_i/n$	σ	: $[\Sigma(x_i - \bar{\bar{x}})^2/(n-1)]^{1/2}$

It is important to note that the standard deviation σ is the "total" standard deviation which include process, sampling, sample preparation and measurement (analysis) standard deviation.

7. Range Chart

As its name implies, this chart monitors the range of a process variable; thus the precision. The vertical axis of this chart represents the range of "two" observations and the horizontal axis represents time. It is useful, for example for monitoring the precision of chemical analysis. In many cases, the samples to be analyzed are not identical, so the mean chart may not be suitable. In this case the range chart will be able to see if the analytical process is under (statistical) control. Figure 3 shows an example of a range chart. It should be noted that the distribution of the range is not symmetrical; the 50% level is $0.845\bar{R}$, the 95% limit is $2.456\bar{R}$ and the 99% limit is $3.27\bar{R}$. Thus:

Central line: $0.845\bar{R}$

UWL : $2.456\bar{R}$

UCL : $3.27\bar{R}$

$\bar{R}$: $\Sigma R/n$

R : $|x_1 - x_2|$

Construction and update of Control Charts

Initially, the control chart can be constructed with a few determinations of the process results, for example, 10 determinations). Once the initial chart has been started, the new data can then be added as they become available. It should be noted that in adding points for the R chart, the condition for obtaining duplicate results must be consistent, i.e. if the duplication is carried out under repeatability condition, it must be always carried out under the same condition.

Since the main purpose of control charts is to see if the process is under control, i.e. to see if at any moment the process is out of control, it is imperative that it should be updated periodically. The frequency of update depends on the nature of the process. The mean can be periodically updated as new data become available, for example by using the moving average method. The length of the period depends on the state of the process. A shorter period is necessary at the initial state and a longer period may be sufficient when the process has reached a steady state. The presence of a trend can be observed visually. Even though the availability of a personal computer at the present time simplifies the task of updating control charts, the updating procedure should be chosen in such away that the resulting control charts remain relatively simple. Updating the mean too frequently will result in a more complicated looking central line. The process variation can be observed by both the magnitude of σ and by the range chart. Both limits of the mean chart and the range chart should also be updated periodically. Visual observa-

tion or statistical test (F ratio test) may be used to determine if these charts require updating.

Practical interpretation of Control Charts

The main use of control charts is to see trends both of precision and of the mean. The probability that a process result will fall above the central line is about 50%. Thus if for any reason these results fall above the central lines by significantly different from 50%, then the operator will be able to detect some change. This change can also be detected by the movement of the moving average mean. The trend of the precision can be observed by the amplitude of the mean chart or by the movement of the mean range of the range chart. The probability that a result will fall above UCL or below LCL is less than 1% (0.05% on each side). Thus if this phenomenon is observed, then a change in the process must have occurred. The probability that a process result will fall outside the warning limits (UWL and LWL) is less than 5%. If it happens, a warning for possible change may be justified. If two consecutive results fall on the same side of the warning limits, then for certain there has been a change in the process. Thus immediate corrective action may be warranted.

References

A. International Standards relevance to the subject:

1. "Statistical Methods", ISO Standards Handbook 3, 2nd edition 1981, International Organization for Standardization, Case Postale 56, Geneva 20, Switzerland.

2. ISO 5725

3. ISO 3534

B. Recommended reading materials:

4. "Statistical Analysis in Chemistry and Chemical Industry", Bennett, C. A. and Franklin, N. L., John Wiley & Sons, Inc., New York.

5. "Introduction to statistical analysis", Dixon, W. J. and Massey, F. J., Mc Graw-Hill Book Company, New York.

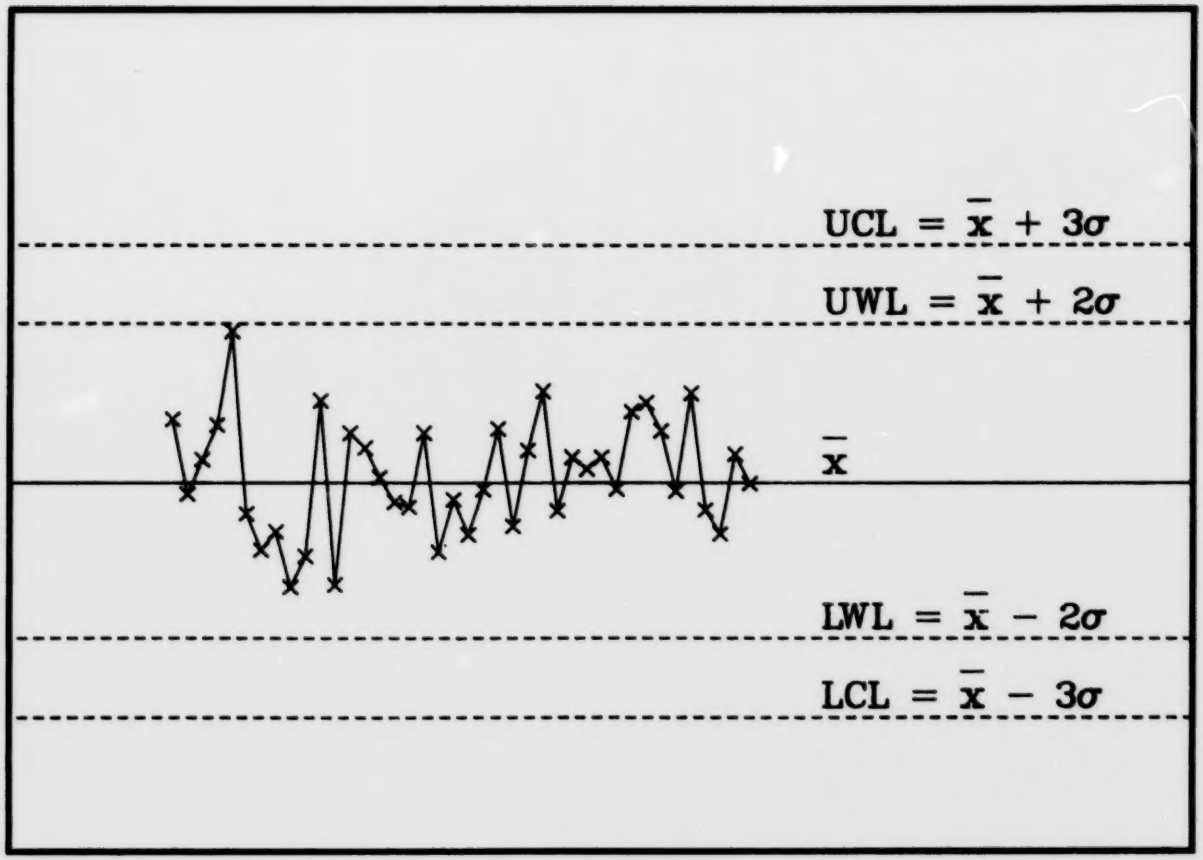

Figure 1. Example of a mean chart showing upper and lower warning and control limits.

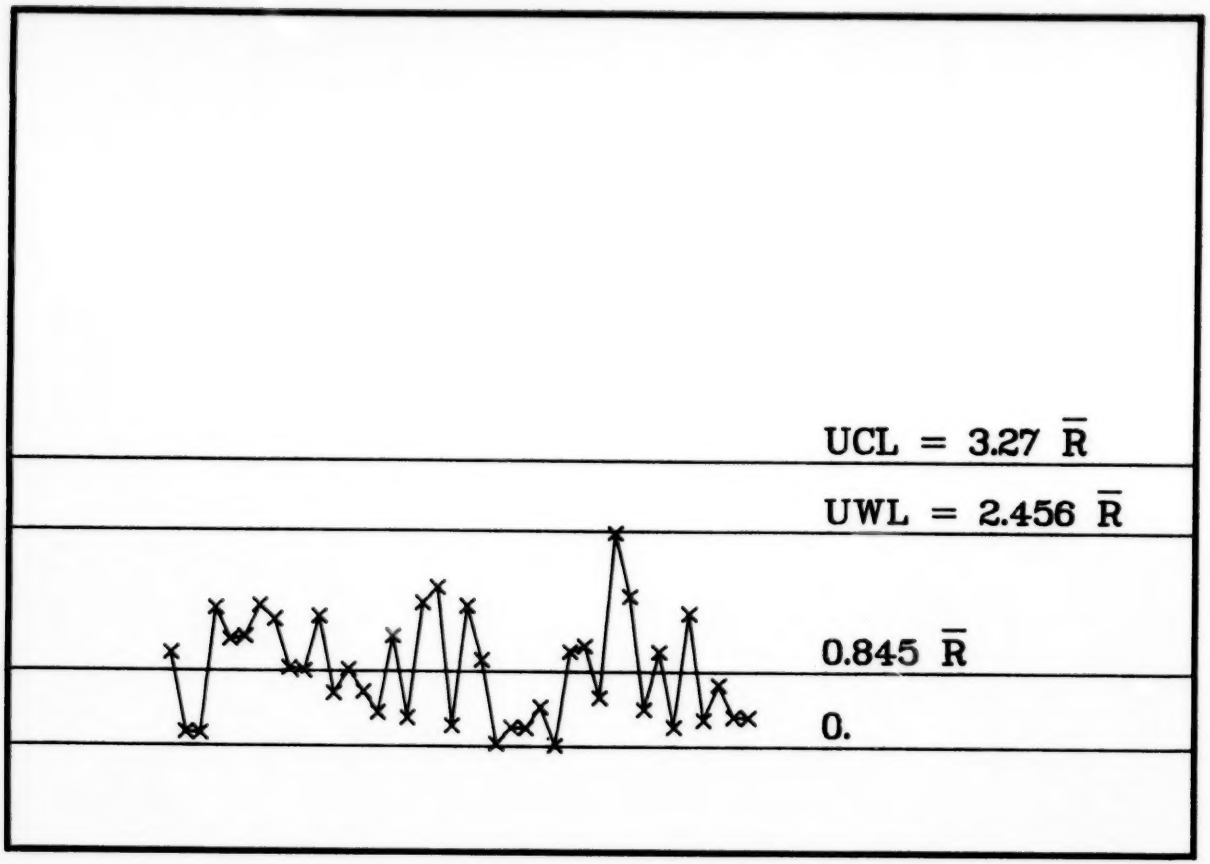

Figure 2. Example of a range chart. Vertical axis is the range of two observations and horizontal axis is time.

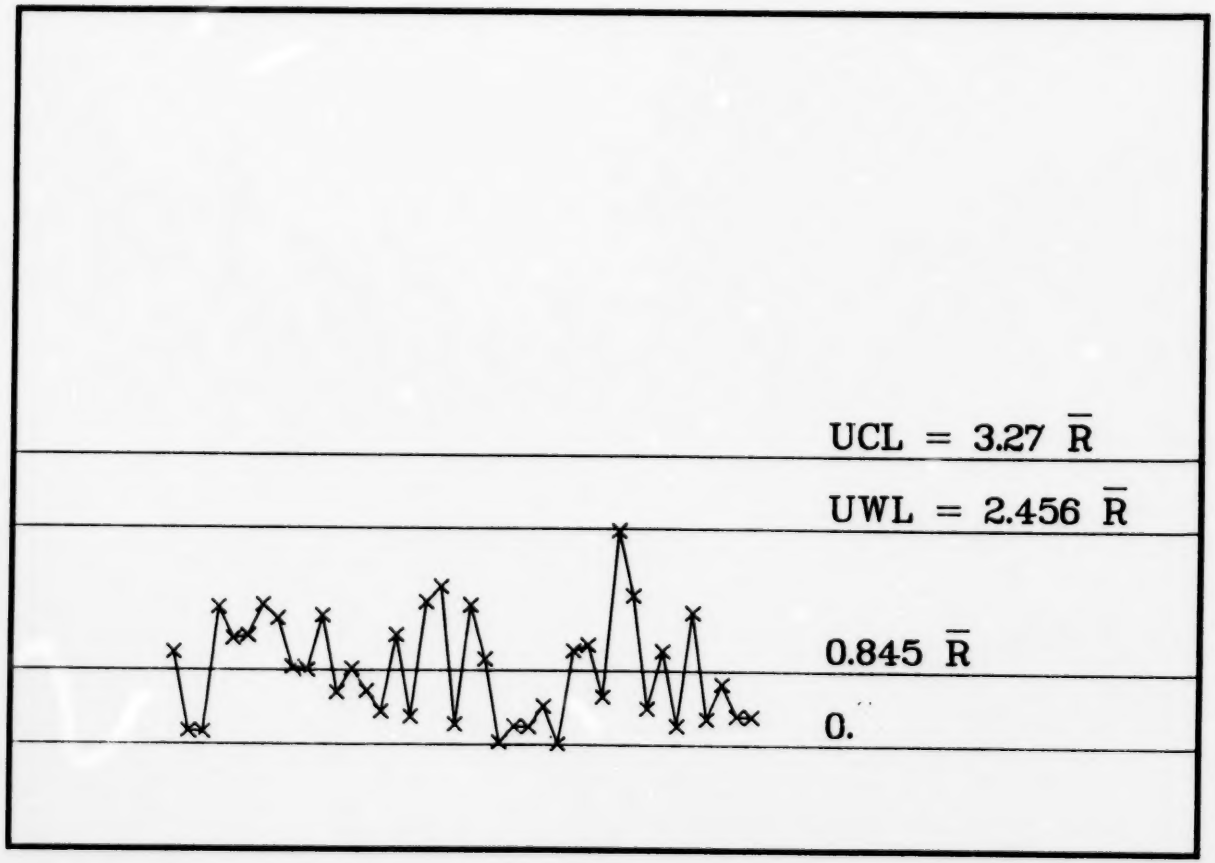

Figure 3. Example of a range chart. Vertical axis is the range of two observations and horizontal axis is time.